Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O_2 supply to the global thermocline

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[1] An analysis of sedimentary nitrogen isotope records compiled from widely distributed marine environments emphasizes the global synchrony of denitrification changes and provides evidence for a strong temporal coupling of these variations to changes in nitrogen fixation as previously inferred. We explain the global coherence of these records by a simple physical control on the flux of dissolved oxygen to suboxic zones and the coupling to fixation via the supply of phosphorus to diazotrophs in suitable environments. According to our hypothesis, lower glacial-stage sea surface temperature increased oxygen solubility, while stronger winds in high-latitude regions enhanced the rate of thermocline ventilation. The resultant colder, rapidly flushed thermocline lessened the spatial extent of denitrification and, consequently, N fixation. During warm periods, sluggish circulation of warmer, less oxygen rich thermocline waters caused expansion of denitrification zones and a concomitant increase in N fixation. Local fluctuations in export productivity would have modulated this global signal. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805); 4267 Oceanography: General: Paleoceanography; 4825 Oceanography: Biological and Chemical: Geochemistry; 4870 Oceanography: Biological and Chemical: Stable isotopes; *KEYWORDS:* isotopes, fixation, denitrification

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1. Introduction

[2] Analyses of marine sediment core samples recovered from a growing number of sites have made it clear that, to first order, sedimentary $\delta^{15}N$ records do not uniformly covary over glacial-interglacial timescales, as do, for example, down core benthic foraminiferal $\delta^{18}O$ records. Instead, down core $\delta^{15}N$ profiles from different parts of the globe vary greatly in both the magnitude and even the sign of change over climatic cycles. In light of the numerous isotopic fractionation effects observed in the modern ocean (see *Sigman and Casciotti* [2001] for a review), many sediment $\delta^{15}N$ records have been interpreted as representing increasingly complex combinations of local processes.

[3] Yet, despite the apparent contrasts between different oceanic regimes, a degree of correspondence has been observed among sedimentary $\delta^{15}N$ records located close to regions of modern water column denitrification (WCD) [*Ganeshram et al.*, 2000; *Kienast et al.*, 2002]. Here we show that these correspondences extend to areas with strong oxygen minima but without present-day WCD activity. Furthermore, when we examine a region dominated by local inputs of bioavailable N by N-fixation as well as those regions which lie between zones of fixation and denitrification, there is evidence for an effective global coupling of the rates of fixation and denitrification, as speculated by other authors [*Ganeshram et al.*, 2002; *Tyrrell*, 1999] but previously uncorroborated by the sedimentary record.

[4] It is proposed here that the link among disparate WCD zones can be parsimoniously explained by global changes in the marine nitrogen cycle that are fundamentally driven by the flux of dissolved oxygen to the major denitrification zones via lateral advection of waters within the permanent thermocline. The term "thermocline" is used here to denote the water masses variously referred to as "central," "mode," or "intermediate," which span the potential density range of ~25 to 27.3 kg m^{-3}, in the sense of *Luyten et al.* [1983], *Slowey and Curry* [1995] and *Karstensen and Quadfasel* [2002]. The base of the thermocline varies between a few hundred meters at high latitudes to over 1000 m depth in the central subtropical gyres. The oxygen flux is physically dependent on the combined effects of the temperature dependence of oxygen solubility and the vigor of thermocline ventilation, crucially influenced by wind and sea-ice processes. All of these factors are linked to the sea surface conditions in the high-latitude source areas where the thermocline is ventilated [*Luyten et al.*, 1983] in the North Pacific, North Atlantic and, most importantly, the Southern Ocean [*Sarmiento et al.*, 2004]. We provide a conceptual model to show how the response of the nitrogen system to

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Table 1. Sedimentary $\delta^{15}N$ Records Shown in This Paper

Core	Location	Water Depth, m	Reference
ODP 722	Arabian Sea (16°37′N, 59°48′E)	2028	*Altabet et al.* [1999]
ODP 887	Gulf of Alaska (54°21.92′N, 148°26.78′W)	3647	this study
NH22P	Mexico (23°31.1′N, 106°31.1W)	2025	*Ganeshram et al.* [2000]
CD 38-02	Peru (14°56′S, 77°04′W)	2525	*Ganeshram et al.* [2000]
SEDORQUA 20bK	Mauritania (25°02′N, 16°39′W)	1445	*Bertrand et al.* [2000]
GeoB 1016-3	Angola (11°46′S, 11°41′E)	3411	*Holmes et al.* [1999]
MD 96-2086	Namibia (25.81°S, 12.13°E)	3606	*Bertrand et al.* [2002]
SO95 17961	South China Sea (8°30.4N, 112°19.9E)	1795	*Kienast* [2000]
MD 84641	eastern Mediterranean (33°02′N, 32°38′E)	1375	*Calvert et al.* [1992]

changes in the dissolved oxygen supply can produce $\delta^{15}N$ records that vary according to a common rhythm, but which differ in regionally distinct ways.

2. Materials and Methods

[5] Downcore $\delta^{15}N$ records have been compiled mainly from the literature, the sources of which are shown in Table 1. The records are presented on their original timescales, as per the cited publications, with no modifications. It is important to note that many of these age models rely exclusively on low resolution $\delta^{18}O$ records; errors of >10 kyr are possible, though these errors are significantly reduced near marine isotope stage boundaries.

[6] A new $\delta^{15}N$ record from ODP Site 887 in the Gulf of Alaska is also included. Samples were freeze dried, ground in an agate mortar, packed in tin cups and measured by combustion using a Carlo Erba NC 2500 elemental analyzer coupled to a Finnigan Mat Delta Plus mass spectrometer, via a Finnigan Mat ConFlo III. The standard deviation of repeat measurements from this core was approximately 0.3‰. The age model from 0 to 34.5 cal kyr is based on correlation of GRAPE records to the site survey core, PAR-87, which has ten radiocarbon dates of planktonic foraminifera. Below this the age model is based on the visual correlation of a low resolution benthic foraminiferal $\delta^{18}O$ record to the *Martinson et al.* [1987] curve [*McDonald et al.*, 1999]. A more complete discussion of the record will be presented elsewhere (E. D. Galbraith et al., manuscript in preparation, 2004).

3. Discussion

3.1. Past Changes in Sedimentary $\delta^{15}N$

[7] The N isotopic ratio of organic matter accumulated on the seafloor provides a tool with which to characterize past states of the marine N budget. Many local processes introduce fractionation of N isotopes from the initial N pool and have been cited as potential contributors to the $\delta^{15}N$ signal recorded in bottom sediments at a given site. Among these are relative nutrient utilization [*Altabet and Francois*, 1994], phytoplankton species effects shown in culture [*Montoya and McCarthy*, 1995], trophic exchanges shown in food web studies [*Minagawa and Wada*, 1984], sea level effects [*Giraud et al.*, 2003] and diagenesis [*Freudenthal et al.*, 2001]. However, it has not been proven that, at a given site, changes in any of these local parameters have large impacts on down core $\delta^{15}N$ profiles over long time periods; the fact that some records show very little change in $\delta^{15}N$ over hundreds of thousands of years despite significant potential for local influences [*Kienast*, 2000] demonstrates that these processes do not necessarily generate significant variability over time. Consequently, it can be reasonably assumed that local factors (although important in determining the absolute magnitude of the $\delta^{15}N$ signal recorded) are probably relatively invariant on millennial timescales for many fixed locations on the seafloor. Sedimentation is a potent averaging mechanism, involving both areal averaging, through the large-scale lateral advection of sinking and sedimented particles (particularly fine-grained organic matter [*Mollenhauer et al.*, 2003]) and temporal averaging through bioturbation and sampling. As a result, only at sites subject to unusually large, sustained changes in relative nutrient drawdown, plankton community structure, or sedimentary environment do these local processes generate impacts on $\delta^{15}N$ that dominate down core profiles.

[8] Many sedimentary $\delta^{15}N$ records are, instead, overwhelmed by temporal variations in the isotopic signature of the regional nitrogen pools that support plankton growth, determined by the relative importance of N fixation and denitrification within the region [*Altabet et al.*, 1995; *Ganeshram et al.*, 2000; *Struck et al.*, 2001]. Because denitrification and N fixation are localized in discrete volumes of the ocean, their isotopic impacts are not evenly distributed. Instead, the ocean will be divisible into those regions in which WCD dominates the isotopic signal, those in which N fixation dominates, and those which receive significant influences from both. We look first to regions with ''denitrification-type'' records.

3.2. Global Changes in Denitrification Over the Past 200 kyr

[9] Water column denitrification currently accounts for 25–60% of the loss of fixed N from the marine system [*Codispoti et al.*, 2001; *Gruber and Sarmiento*, 1997]; the remainder is lost predominantly by sedimentary denitrification. Strong isotopic fractionation during the incomplete bacterial reduction of NO_3^- to N_2 in the water column leaves a residual NO_3^- pool enriched in ^{15}N. As a result, the $\delta^{15}N$ of nitrate ($\delta^{15}N_{nitrate}$) in the immediate vicinity of WCD zones is higher than the global average $\delta^{15}N_{nitrate}$ of ~5‰ [*Sigman et al.*, 1999], typically 9 to 18‰ [*Brandes et al.*, 1998; *Voss et al.*, 2001]. This isotopically heavy NO_3^- is mixed upward or welled up, incorporated into phytoplankton and transferred to the sediment, which thereby records a high $\delta^{15}N$ signal. WCD is confined to regions where dissolved oxygen concentrations are below 5 μmol/kg [*Codispoti et al.*, 2001] (Figure 1), which currently includes

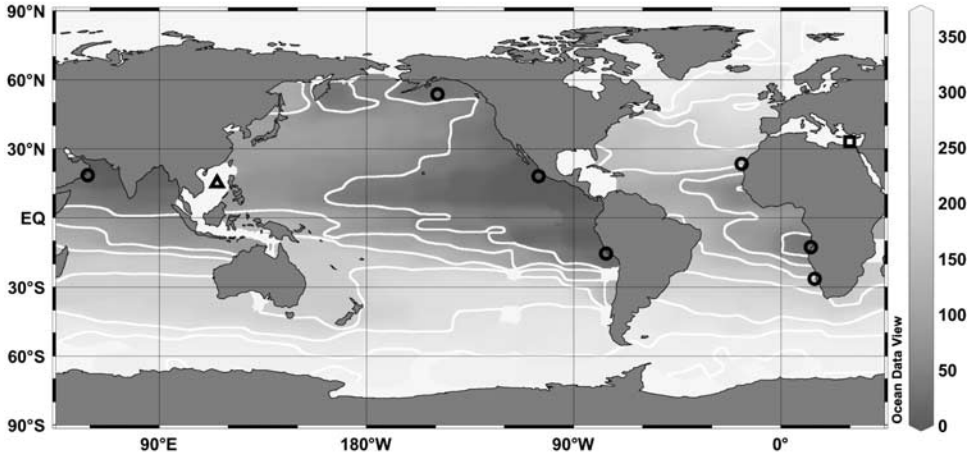

Figure 1. Dissolved O_2 (μmol/kg) on the 27.0 σ_θ isopycnals; white contour lines are at 50 μmol/kg intervals. This potential density surface lies near the core of the AAIW and intersects the middepths of the world's WCD zones: the eastern tropical North Pacific, eastern tropical South Pacific, and Arabian Sea. Also visible are the low O_2 zones of Angola-Benguela, NW Africa, and the Subarctic Pacific. The locations of cores discussed in this paper are shown according to their dominant isotopic influence, as discussed in the text, indicated by a circle (denitrification), square (fixation), and triangle (mixed). Oxygen minima zones form where high oxidant demand, generated by the respiration of sinking organic matter from highly productive surface waters, coincides with low rates of oxygen renewal as determined by water mass circulation. Figure generated with Ocean Data View (R. Schlitzer, Ocean Data View, 2003; see http://www.awi-bremerhaven.de/GEO/ODV) with the WOCE one-time data set.

the eastern tropical North Pacific (ETNP), eastern tropical South Pacific (ETSP) and the Arabian Sea (AS). Two other regions, the Subarctic Pacific and the Angola-Benguela system, are only marginally more oxygenated, with [O_2] as low as 18 μmol/kg reported in both regions during the World Ocean Circulation Experiment (WOCE online data set). Denitrification can occur throughout the upper 1 km of the water column, although the most intense denitrification intervals are found between 150 and 500 m [*Codispoti et al.*, 2001], the upper central portion of the permanent thermocline, as defined above. Because the locations of these poorly ventilated cul-de-sacs are defined by large-scale gyre circulation, it is unlikely that their gross distribution has changed over the Quaternary.

[10] Previous compilations of sedimentary $\delta^{15}N$ records from regions of modern WCD in the eastern Pacific and the Arabian Sea [*Ganeshram et al.*, 2000] have shown patterns of enhanced denitrification during interglacials and reduced denitrification during glacials. We extend this correspondence to $\delta^{15}N$ records near the remaining low oxygen zones: those of the Subarctic Pacific and western Africa (Figure 2). When this is done, a number of strongly coherent characteristics over the past 200 kyr emerge. In particular, all have high $\delta^{15}N$ during interglacial periods, both during the 20 kyr since the Last Glacial Maximum (LGM) and during the previous interglacial, 135 to 115 kyr ago. Particularly consistent is an early Holocene peak, common to all records in which the core top was recovered. Also, pronounced minima occur during cold periods, particularly between ~75 and ~60 kyr ago. It is important to note that the chronologies of these records are all based on their original foraminiferal $\delta^{18}O$ timescales; in order to present an unbiased comparison, no attempt has been made to improve temporal agreement by "tuning" the $\delta^{15}N$ records (although doing so could undoubtedly improve the visual agreement). In spite of our reluctance to fine tune the published records, and as noted previously, it is likely that at least the isotope stage boundaries can be reasonably well correlated, providing some confidence in the identification of the stages themselves and the coherence of the isotopic records displayed.

[11] Intervals of high $\delta^{15}N$ in sediments that underlie regions of modern WCD clearly indicate periods of enhanced interglacial denitrification, as previously established [*Altabet et al.*, 1995; *Ganeshram et al.*, 2000, 1995]. These have been linked to both climatic changes and to fluctuations in atmospheric concentrations of the radiatively active gases N_2O and CO_2 [*Altabet et al.*, 2002; *Suthhof et al.*, 2001]. However, the explanation for the correspondence observed in the other records is less obvious.

[12] The new results from the Gulf of Alaska (Figure 2) show the presence of simultaneous $\delta^{15}N$ variations, of similar magnitude, far from the nearest recognized location of modern WCD (the ETNP). This is the first deep-sea location (3647 m water depth) we are aware of that yields a $\delta^{15}N$ record that parallels recognized climate-related changes in denitrification. Drastic changes in productivity, evident as rapidly deposited diatom oozes that punctuate a background of hemipelagic mud [*McDonald et al.*, 1999] (indicated on Figure 2) are associated with only minor fluctuations in $\delta^{15}N$, making a local ecosystem or diagenesis-related explanation for the glacial-interglacial scale down core variability unlikely, while the location precludes an influence of sea level/shelf interactions [*Bertrand et al.*, 2000]. Contemporaneous variations in $\delta^{15}N$ on the western margin of North America recorded as far north as the

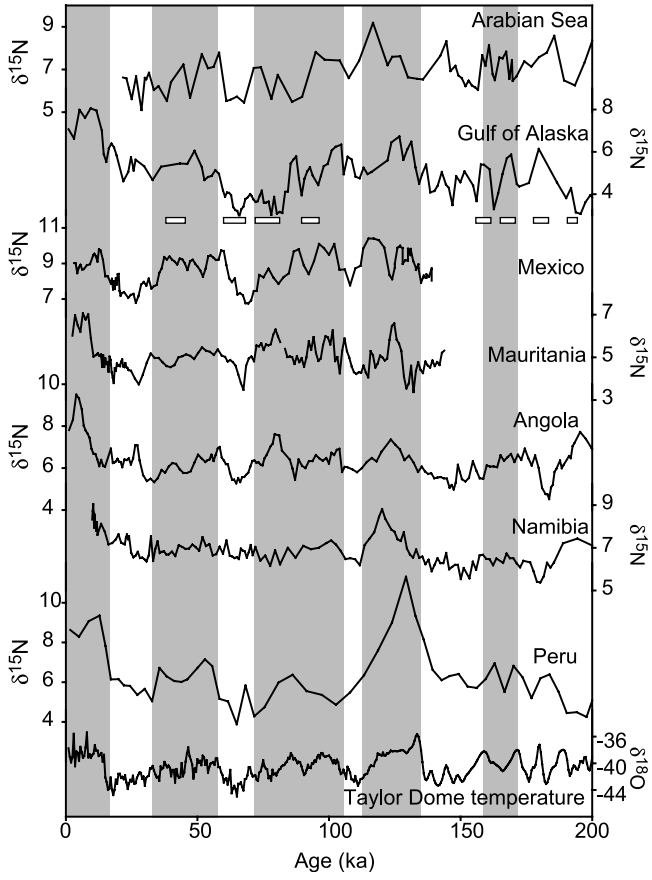

Figure 2. Sedimentary $\delta^{15}N$ records from areas of present and/or potential WCD for the last 200 kyr. Although the records are by no means identical, they reveal a number of striking similarities. Particularly evident are two maxima (within the last 18 kyr and between 135 and 115 kyr ago) and two minima (during 74–59 kyr ago and 115–108 kyr ago), although there are numerous other similar features. It is important to note that all data are plotted versus the original age models as provided by the authors, with no alteration: Gulf of Alaska [*McDonald et al.*, 1999], Arabian Sea [*Altabet et al.*, 1999], Mazatlan [*Ganeshram et al.*, 2000], Mauritania [*Bertrand et al.*, 2000], Angola [*Holmes et al.*, 1999], Namibia [*Bertrand et al.*, 2002], and Peru [*Ganeshram et al.*, 2000]. All timescales are based on $\delta^{18}O$-foraminifera, and therefore the age models may have large errors, on the order of 10^4 years. The features discussed are generally synchronous within this error. White rectangles indicate the locations of rapidly deposited diatom-rich layers in the Gulf of Alaska core that interrupt the background of hemipelagic clay without any consistent impact on $\delta^{15}N$. Also shown is a record of $\delta^{18}O_{ice}$, a proxy for atmospheric temperature, from the Taylor Dome ice core, Antarctica [*Masson et al.*, 2000; *Grootes et al.*, 2001].

Oregon margin, where WCD does not occur today, have been shown to result from the advection of isotopically heavy nitrate from the ETNP WCD zone [*Kienast et al.*, 2002; *Liu and Kaplan*, 1989; *Pride et al.*, 1999], proving that substantial regional signals can emanate beyond a relatively small WCD zone; thus, the Gulf of Alaska $\delta^{15}N$ signal may be due solely to advected high $\delta^{15}N_{nitrate}$ from the ETNP. However, given that the amplitude of the Gulf of Alaska signal (2–3‰) is comparable to those observed on the Oregon margin [*Kienast et al.*, 2002], despite the much greater distance from the ETNP, it seems unlikely that this can be the sole explanation. An additional contribution has potentially come from local denitrification in the oxygen minimum zone of the Subarctic Pacific that has fluctuated in its local intensity. The fact that denitrification has not previously been described in the region may indicate that it has been overlooked, or more likely, that it waned following the early Holocene, due to factors discussed below, and is no longer operational. This is consistent with core top values >1‰ lower than those of the early Holocene maximum, and with a well-documented deglacial period of widespread oxygen deficiency throughout the North Pacific [*Ohkushi et al.*, 2003; *Zheng et al.*, 2000].

[13] An alternative explanation is that the degree of denitrification in the ETNP exerts a strong control on the availability of NO_3^- to the Subarctic Pacific (presently an HNLC region), such that during periods of intense denitrification the reduced NO_3^- supply to the Gulf of Alaska causes an increased degree of relative NO_3^- utilization. The lack of correlation between % C_{org} and $\delta^{15}N$ in this core (r^2 = 0.03, not shown) supports the inference that variations in $\delta^{15}N$ are linked to the nitrate supply rather than to changes in local productivity altering the relative degree of uptake from a temporally invariant NO_3^- supply (as would occur in the case of, for example, Fe fertilization of this HNLC region). In either case, the Gulf of Alaska record strengthens the case for widespread loss of fixed N from the North Pacific during warm periods, and for the regional extent of the resulting isotopic signal.

[14] The west African records present a similar situation. Although it has previously been suggested that small amounts of WCD occur in the Angola-Benguela system off southwestern Africa [*Dittmar and Birkicht*, 2001; *Tyrrell and Lucas*, 2002], most sedimentary $\delta^{15}N$ records from western Africa have been interpreted as dominantly reflecting changes in local relative nitrate utilization related to wind-driven upwelling dynamics [*Freudenthal et al.*, 2002; *Holmes et al.*, 1999; *Martinez et al.*, 2000]. Nonetheless, it has recently been suggested that enhanced periods of denitrification in the past may have played a role in generating variability in sediment $\delta^{15}N$ records from coastal Namibia [*Lavik*, 2002]. Given the near zero oxygen concentrations in modern thermocline waters of the Angola basin, it seems reasonable that WCD may have occurred there in the past, and perhaps also in the low oxygen zone off NW Africa. If so, the lack of significant WCD and the relatively low $\delta^{15}N$ of late Holocene sediments in the region could be explained by a decline of local denitrification following the early Holocene, as suggested above for the Gulf of Alaska and as discussed further below. The observed anticorrelation between $\delta^{15}N$ and C_{org} on the SW African margin [*Holmes et al.*, 1999] is consistent with this interpretation, as high rates of WCD could reduce the available NO_3^-

concentration, limiting C export during production of high $\delta^{15}N_{nitrate}$, and vice versa. Hence we propose that the majority of large $\delta^{15}N$ variations on glacial-interglacial timescales reflect changes in WCD activity on the African margin. Again, the $\delta^{15}N$ increases could be attributed to an intensification of remote denitrification zones and an ensuing reduction in nitrate concentrations on the African coast, leading to higher relative nitrate utilization. In either case, these records testify that changes in denitrification have been broadly global and coordinated.

[15] In summary, despite the potential for obfuscation by local processes, sedimentary $\delta^{15}N$ fluctuations chronicle broadly synchronous glacial-interglacial increases and decreases in WCD in all oceanic regions with oxygen deficient intermediate waters. In general, it appears that WCD is less active during cold periods, more active during warm periods, and most active when the ocean is warming after a cold period. Were the global aggregate WCD rate to have changed in the absence of corresponding changes in N fixation, the isotopic signature of the global average $\delta^{15}N$ pool would be expected to have followed the magnitude of WCD [*Brandes and Devol*, 2002] and all $\delta^{15}N$ records would parallel those from WCD zones. The fact that they do not provides important information on the operation of the marine N system, as discussed next.

3.3. Coupling of N Fixation to Denitrification

[16] High denitrification rates in geographically confined regions of the subsurface generate waters depleted in N, i.e., with a relatively low N:P, clearly observed as regions of negative N* in the modern ocean [*Gruber and Sarmiento*, 1997]. Nitrogen fixation counters the loss of N by generating biomass with high N:P [*Karl et al.*, 1997] in shallow, warm, stratified surface waters with sufficient micronutrient input [*Carpenter et al.*, 1997; *Falkowski*, 1997], restoring the water mass N:P to near (or locally above) the 16:1 "Redfield" ratio. The long residence time of marine P (20–30 kyr [*Delaney*, 1998]) is generally thought to limit the potential for glacial-interglacial changes in P inventory, and certainly rules out rapid change; thus, it has long been considered the ultimate limiting nutrient on multimillennial timescales [*Ganeshram et al.*, 2002; *Tyrrell*, 1999]. Nitrogen fixation has thus been regarded as a process that maintains a biologically suitable N:P in the face of N losses from denitrification. Indeed, given a preindustrial rate of total global denitrification of $\sim$0.25 Pg N yr^{-1}, a terrestrial source to the oceans of $\sim$0.05 Pg N yr^{-1} and a global inventory of $\sim$1000 Pg N [*Gruber and Sarmiento*, 1997], the oceans would be devoid of N in 5 kyr in the absence of N fixation.

[17] However, the spatial separation of these two processes limits the ability of fixation to keep up with denitrification [*Codispoti et al.*, 2001]; the response is not immediate, and the coupling is therefore imperfect. The highest N:P will be found in areas that receive a significant N input from fixation, while elsewhere partially denitrified waters are bound to be N deficient. Thus during times of high denitrification rates, N limitation will develop throughout large regions of the surface ocean where N fixation is prohibited by other factors [*Codispoti*, 1989; *Falkowski*, 1997]; meanwhile, during times of less extensive denitrification, N limitation will be relieved and global N:P will approach a higher value, as discussed by *Ganeshram et al.* [2002].

[18] We propose that the response of regions capable of supporting N fixation to enhanced denitrification occurs via the supply of excess P to such regions. When thermocline waters that have undergone denitrification (low N:P) well up, NO_3^- is depleted first, leaving excess P. This can be seen in the modern ocean, in that surface waters of the ETNP, ETSP and Arabian Sea become exhausted in nitrate during high production periods while 0.2–0.7 μmol/kg phosphate remains [*Codispoti*, 1989; *Fanning*, 1992]. The nitrate-depleted surface waters of the ETSP present a particularly good example, maintaining high concentrations of unused phosphate (>0.5 μM) over thousands of km. These high P waters remain relatively barren until advected, potentially across long distances, to regions with warm (>20°C), stratified surface waters, with sufficient micronutrient input (including Fe), where they can fuel the growth of N fixers [*Carpenter et al.*, 1997], known often to be limited by P in the modern world [*Mills et al.*, 2004; *Sanudo-Wilhelmy et al.*, 2001]. As a result, N may become more limiting in nitrate-supported upwelling zones while fixation-supported communities, potentially far from denitrification zones, will enjoy relatively high production.

[19] In contrast, when denitrification rates are low, upwelling waters will develop higher N:P ratios. As a result, associated biota will be able to completely utilize P with the upwelled NO_3^- supply, such that very little P is available for nitrogen fixers. This would lead to high productivity in and around upwelling zones and very low productivity in N fixation basins. Because N limitation would be alleviated in most of the ocean, overall productivity would likely be higher during these cold periods. This scenario suggests an interesting relationship with Fe-limitation of N fixers: if dustborne Fe supply is reduced during warm periods [*Falkowski*, 1997] when WCD is most active, Fe could limit N-fixation in many regions during the periods when it is most needed. On the other hand, abundant Fe supply during cold periods may have little effect on the N inventory, as low P-availability would limit N fixation under cold, windy conditions due to diminished WCD.

3.4. Isotopic Record of the Fixation Response

[20] Because of the spatial partitioning of WCD and N fixation between localized thermocline waters and warm stratified basins, respectively, we can look to sedimentary $\delta^{15}N$ records in potential N fixation basins for fixation responses corresponding to changes in denitrification, as postulated by *Ganeshram et al.* [2002]. Because newly fixed N is isotopically similar to atmospheric N ($\sim$−1‰; *Brandes and Devol* [2002], fixation should leave an imprint of low $\delta^{15}N$ in sediments. However, because N fixation is dispersed across large expanses of tropical and subtropical seas, the isotopic signal will be more dilute than the strongly localized signals of WCD zones. An exception to this circumstance would be found in regions with permanently

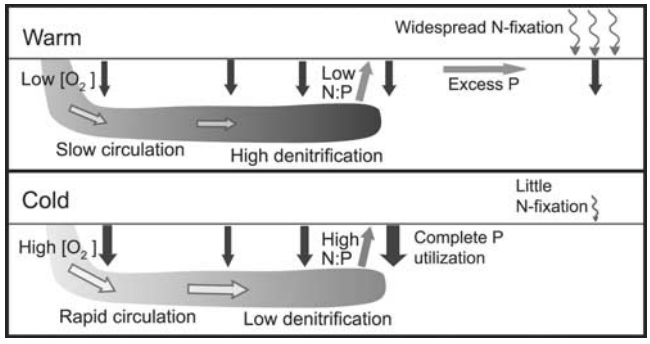

Figure 3. Schematic illustration of high-latitude surface control on denitrification and the fixation response. Downward pointing arrows represent export production. Intermediate waters that form (top) under warm conditions carry relatively less O_2 and circulate more slowly, thus encouraging suboxia and denitrification. Under cold conditions (bottom), high dissolved [O_2] and rapid circulation reduce the extent of suboxia, impeding denitrification. Denitrification zones remove fixed-N from intermediate waters, exporting low N:P waters which, when upwelled, produce N-limited communities; excess-P is then advected to regions with warm, stratified surface waters where it fuels nitrogen fixation. When high O_2 inhibits denitrification, high N:P ratios in upwelling zones allow complete utilization of P to the detriment of N-fixation communities elsewhere.

low concentrations of nitrate, where local diazotrophy would constitute the primary N supply. Unfortunately, there are no published $\delta^{15}N$ records from oligotrophic gyres with which to test this hypothesis, because the sediments in such regimes accumulate slowly (generating low resolution records) and often lack foraminiferal age models (because of their great water depth).

[21] However, the eastern Mediterranean is a potentially sensitive region in which to look for changes in N fixation in response to a variable P supply. The deep waters are isolated due to the 500 m deep Straits of Sicily, such that only shallow waters are able to exchange with the western Mediterranean and, ultimately, the North Atlantic. In the modern antiestuarine situation, shallow (<100 m) nutrient-depleted waters flow into the eastern Mediterranean, maintaining its oligotrophic status and strong P limitation [*Krom et al.*, 1991]. Although the N:P in much of the Mediterranean is already quite high, the surface conditions are apparently so conducive to N fixation that up to 30% of modern new production is supported by diazotrophic N [*Gruber and Sarmiento*, 1997; *Pantoja et al.*, 2002; *Struck et al.*, 2001]. This, combined with the minimal supply of high $\delta^{15}N$-nitrate from outside the basin, leads to the relatively low $\delta^{15}N$ of surface sediments in the eastern Mediterranean (4–4.5‰). According to the reasoning presented above, the periods of enhanced denitrification in the eastern Atlantic should have generated low N:P waters which would have spread throughout the region, largely through subsurface circulation. These N-poor waters would have been mixed into the Mediterranean, either at surface or at depth (depending on the circulation regime at the time), encouraging N limitation and, thus, stimulating N fixation with low $\delta^{15}N$.

[22] As shown in Figures 3 and 4, the $\delta^{15}N$ record from the eastern Mediterranean is entirely consistent with this scenario. All of the $\delta^{15}N$ maxima on the west African margin correspond to $\delta^{15}N$ minima in the eastern Mediterranean. This diametric opposition can be explained as an overall decrease in the availability of fixed N relative to P and a corresponding increase in N fixation in the ideally suited environment of the Mediterranean. The close relationship between the isotopically light $\delta^{15}N$ sapropels and hydrographic changes in the basin [*Calvert and Fontugne*, 2001; *Struck et al.*, 2001] may reflect the need for an abundant relative P supply (due to remote denitrification) to promote extensive N fixation, as well as a suitable local physical environment. Precessionally driven, monsoon-related changes in precipitation have been shown to impact the evaporative balance of the Mediterranean, reducing the antiestuarine character of the basin during moist periods; we suggest that the difference between the poorly developed "ghost" sapropels [*Calvert and Fontugne*, 2001] and the well-developed sapropels characterized by low $\delta^{15}N$ is the externally controlled relative availability of P. As such, the sapropels present a particularly clear example of the direct response of nitrogen fixers to global denitrification

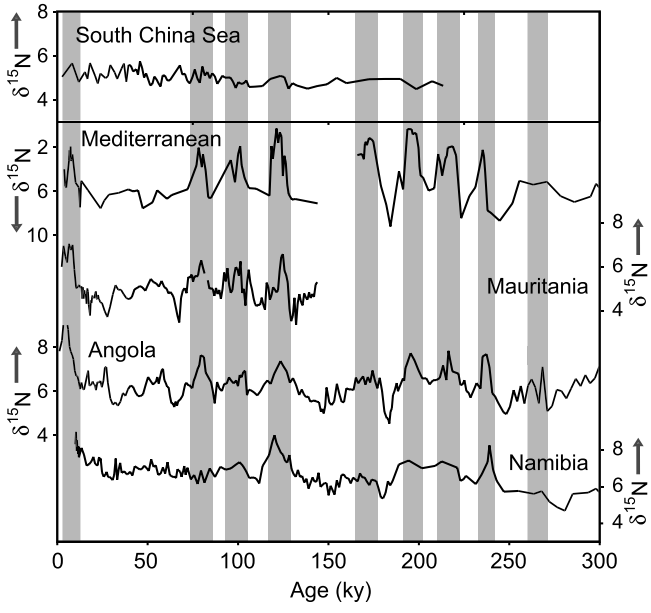

Figure 4. Sedimentary $\delta^{15}N$ records from fixation, denitrification and well-mixed areas. Denitrification off W Africa is indicated by the $\delta^{15}N$ records of Mauritania, Angola, and Namibia, as discussed in the text. The eastern Mediterranean [*Calvert et al.*, 1992] records low $\delta^{15}N$ (note reversed axes), indicating nitrogen fixation, during the same periods as high denitrification is recorded on the African margin. Sedimentary $\delta^{15}N$ records from the South China Sea [*Kienast*, 2000] are relatively invariant over the same time period, suggesting that this is a region of globally well-mixed N, which does not register changes in fixation or denitrification.

rates, communicated by the advection into the basin of relatively P-rich waters.

[23] This interpretation is similar to that of *Struck et al.* [2001], who also invoked enhanced nutrient supply with N-limitation leading to N-fixation during sapropel formation; however they suggested that the denitrification took place within the Mediterranean itself, requiring water column suboxia, and incompatible with the emerging view of sapropel anoxia as being restricted to a blanket at the sediment-water interface [*Casford et al.*, 2003]. The enhanced runoff during sapropel formation could also promote P supply, but would simultaneously provide additional N and seems therefore less likely to promote the massive amounts of N-fixation required to explain the $\delta^{15}N$ record. Of course, correlation is not proof of causation, and the inference that high rates of denitrification in the eastern Atlantic could contribute to sapropel formation needs to be tested further.

3.5. Mixed WCD/Fixation $\delta^{15}N$ Records

[24] The arguments presented here support the inference of *Ganeshram et al.* [2002] that the global aggregate rates of both WCD and N fixation covary over glacial-interglacial time periods. These changes produce symmetrically opposing isotopic signals in WCD dominated (high $\delta^{15}N$) and N fixation (low $\delta^{15}N$) regions. Because of the antagonistic relationship between these influences, globally synchronous variations of both should define geographically intermediate regions with less temporal variability in $\delta^{15}N$, in the absence of unusually strong local effects.

[25] In keeping with this prediction, $\delta^{15}N$ records from many regions away from oxygen minimum zones show little or no glacial-interglacial variability. In particular, most records from the South China Sea [*Kienast*, 2000; *Tamburini et al.*, 2003] (Figure 4) and the North Atlantic [*Huon et al.*, 2002] show nearly invariant $\delta^{15}N$ records over the last 200 kyr. Also, $\delta^{15}N$ records from the Southern Ocean show either little glacial-interglacial change [*Robinson et al.*, 2004] or a pattern clearly unlike that of the denitrification records [*Francois et al.*, 1997; *Sigman et al.*, 1997]. We note that the recently published $\delta^{15}N$ record of ODP Site 1144, from a drift deposit near the connection of the South China Sea with the open Pacific [*Higginson et al.*, 2003] shows some degree of variability (<2.5‰) which has been construed as reflecting glacial-interglacial changes; however, based on sedimentological data, we suspect that the complex sediment mixing dynamics incorporated in the creation of this drift deposit are responsible for many elements of this $\delta^{15}N$ record and its difference from the nearby piston core SO95 17940 [*Kienast et al.*, 2003]. The seven other published $\delta^{15}N$ records of *Kienast* [2000] and *Tamburini et al.* [2003], representing diverse sedimentary environments throughout the South China Sea, do not display significant glacial-interglacial variability, and show that, on the whole, the isotopic signature of nitrogen in the basin has remained constant within ±1‰ over the past two glacial cycles. This represents a strong constraint on the variation of global average $\delta^{15}N$ over time: the lack of glacial-interglacial $\delta^{15}N$ changes in such regions is difficult to reconcile with whole ocean changes in aggregate WCD rates unless these changes are directly matched by changes in N fixation rates. In other words, because fixation supplies isotopically light N to replace the isotopically light N removed through WCD [*Brandes and Devol*, 2002], the ratio of fixation:WCD must have remained roughly constant during the late Quaternary in order for a global isotopic balance to have been maintained over periods significantly longer than 10^3 years. Additional sedimentary $\delta^{15}N$ records, spatially remote from both potential WCD and N-fixation basins, are required to test the robustness of this global isotopic balance.

[26] We turn now to the underlying cause driving these changes in the nitrogen cycle. Since it is improbable that simultaneous variations in WCD in the Pacific, Atlantic and Indian Oceans (Figure 2) could have occurred fortuitously through local processes, we propose a simple global mechanism.

3.6. Surface Ocean Link to Global Denitrification

[27] WCD occurs in the small fraction of the ocean (~0.1% by volume) in which oxygen has been almost completely consumed by the respiration of organic matter. Only in regions of the permanent thermocline (150–800 m) with relatively low rates of oxygen supply, which have been exposed to high oxidant demand (OxD) due to the heterotrophic respiration of abundant sinking organic matter, does this happen in the modern ocean (Figure 1). Elsewhere, dissolved oxygen is always present in concentrations greater than 5 μmol/kg, which inhibits WCD.

[28] Virtually all WCD takes place in waters in the density range σ = 26.3–27.2 that are laterally ventilated to some degree by mode and intermediate waters of similar density formed at high latitudes [*Luyten et al.*, 1983; *Russell and Dickson*, 2003; *Sarma*, 2002]. The most important of these are cold, relatively low-salinity waters from the Southern Ocean: the intimately linked Subantarctic Mode Water and Antarctic Intermediate Water, which together span the range σ = 26.0–27.4, are ventilated at the rate of $\sim 80 \times 10^6$ m^3 s^{-1} [*Sloyan and Rintoul*, 2001] and are hereafter collectively referred to as SAMW-AAIW. Because the SAMW-AAIW is of the greatest global importance, providing a dominant input of waters to the thermoclines of the Arabian Sea [*Olson et al.*, 1993], the ETSP [*Toggweiler et al.*, 1991], and the SE Atlantic [*You*, 2002], as well as making a contribution to the ETNP [*Talley*, 1999], we focus our attention on it in this discussion, though other middle- to high-latitude intermediate water sources (particularly the North Pacific and North Atlantic Intermediate Waters) would be expected to follow most of the same general trends.

[29] SAMW-AAIW leaving the high-latitude southern Pacific today, for example, contains roughly 250 μmol/kg O_2 [*Russell and Dickson*, 2003]. As it circuits the subtropical gyre beneath the surface layer, respiration of sinking organic matter provides an OxD that gradually consumes dissolved O_2. While most of this water will well up or mix with more oxygen-rich water masses before the O_2 is fully depleted, a small fraction of this water will follow a path of high OxD. In any region where the total OxD exceeds ~245 μM O_2 equivalent, the suboxic threshold will be

passed and denitrification will ensue. Nitrate is slightly more efficient as an electron acceptor on a mol:mol basis than O_2 (5:4), but nonetheless the concentration is much lower, at most about 45 μmol/kg in intermediate depths. Yet, despite the low concentration, denitrification never goes to completion in the modern open ocean water column (though it does in some restricted basins and in all organic-rich sediments). At most, WCD currently consumes 12–16 μmol/kg NO_3^- [*Brandes et al.*, 1998; *Voss et al.*, 2001], roughly a third of the nitrate available. This means that even those thermocline waters that have undergone the highest integrated OxD in the open ocean have >90% of their oxidant needs met by oxygen. It follows that the presence (or absence) of WCD activity is extremely sensitive to both the dissolved oxygen supply and OxD in all thermocline waters that have dissolved oxygen concentrations near zero.

[30] Greater OxD through increased local export productivity, driven by enhanced upwelling, has often been invoked as an explanation for past variations in WCD [*Altabet et al.*, 1995; *Ganeshram et al.*, 2000]. Although high rates of export productivity are unquestionably important in generating WCD zones, the relevant issue for this discussion is whether or not glacial-interglacial changes in productivity are sufficiently large (and sufficiently uncorrelated with the thermocline O_2 supply) to dominate the WCD changes on multimillennial timescales. The following lines of reasoning lead us to suspect that the oxygen supply term commonly dominates the WCD balance on these (and perhaps shorter) timescales.

[31] It has recently been pointed out that productivity increases lag the sedimentary $\delta^{15}N$ enrichments on the western Mexican margin [*Kienast et al.*, 2002], while $\delta^{15}N$ and productivity proxies in the Angola Basin are actually anticorrelated [*Holmes et al.*, 1999]. Meanwhile, productivity changes in the ETNP over the last 140 kyr, reconstructed from biogenic Ba data, are insufficient to drive the changes in bottom water oxygenation recorded by redox-sensitive trace metals [*Nameroff et al.*, 2004]. In the Arabian Sea, paleoceanographic studies have alternately argued in favor of productivity dominated control and ventilation control of thermocline oxygen concentrations [*Altabet et al.*, 1999; *Reichart et al.*, 2002; *Schulte et al.*, 1999; *Suthhof et al.*, 2001] in spite of the fact that *Olson et al.* [1993] showed that the presence of low-oxygen waters derived from SAMW-AAIW maintained the modern WCD. Furthermore, new work by *Sarma* [2002] shows that increased monsoon-driven upwelling in the modern Arabian Sea enhances productivity (and thus OxD) but simultaneously draws in more shallow thermocline water from roughly those depths that host the maximal rates of WCD (150–400 m). This replenishes the thermocline O_2 at a rate proportional to the rate of nutrient supply to the surface [*Sarma*, 2002]; therefore, changes in the nutrient:O_2 ratio of subsurface waters advected from the south would be expected to have a greater impact on water column oxygenation than would changes in upwelling rates. Because all the potential WCD-hosting upwelling zones in question draw waters up from the depths of the most intense oxygen minimum zone, this mechanism should hold true for all of them.

[32] These reasons, coupled with the globally coherent character of $\delta^{15}N$ shifts on glacial-interglacial timescales, lead us to believe that local productivity variations, although undoubtedly important, are not the primary control on the temporal variability of water column suboxia over glacial-interglacial cycles. Instead, local productivity variations modulate the fundamental signal of physically controlled changes in the dissolved O_2 supply. Excluding oxygen consumption during transit of subsurface waters, the supply of O_2 to thermocline waters is essentially a function of two variables: the [O_2] when the water mass leaves the surface, and the rate at which thermocline waters are flushed. As we discuss next, both of these factors are likely to favor higher O_2 supply during glacial periods.

3.7. Climatically Driven Changes in O_2 Supply

[33] The solubility of O_2 in seawater is strongly dependent on temperature, with solubility increasing rapidly as the temperature nears the freezing point. At the same time, the degree of O_2 saturation is dependent on the efficiency of wind mixing in the formation region; poor mixing limits the modern SAMW-AAIW initial [O_2] to roughly 50 μmol/kg below saturation [*Russell and Dickson*, 2003]. Paleoceanographic evidence shows that the surface of the Southern Ocean cooled by 4–5°C during the LGM [*Mashiotta et al.*, 1999], while proxies of thermocline water temperature are consistent with a glacial SAMW-AAIW that was 4–5°C colder [*Herguera et al.*, 1991; *Lynch-Stieglitz and Fairbanks*, 1994; *Matsumoto et al.*, 2002] and a glacial NAIW that was 4°C colder [*Slowey and Curry*, 1995]. A 4°C temperature decrease corresponds to an increase in oxygen saturation of ~32 μmol/kg. Meanwhile, dust records have been interpreted as reflecting increased windiness during glacial periods [*Petit et al.*, 1999], which would have driven the initial [O_2] of SAMW-AAIW toward saturation. Combining the temperature effect with some degree of enhanced saturation suggests an increase in initial [O_2] during glacial periods of 30 to 80 μmol/kg above the modern value, an increase of 12 to 32%. Given that the most intense modern WCD zones require an increase in [O_2] of only 20 μmol/kg in order to shut down denitrification altogether, this change in surface ocean conditions is capable of providing a first-order control on global intermediate water [O_2] and, consequently, the extent of global WCD over glacial-interglacial timescales.

[34] The rate of SAMW-AAIW formation is also likely to have been generally higher during glacial periods. Stronger Southern Hemisphere high-latitude winds would have enhanced Ekman convergence, driving more cold, low salinity surface water northward into the permanent thermocline [*Karstensen and Quadfasel*, 2002]. An abundant supply of cool, low salinity surface water appropriate for subduction would have been ensured by the glacially enhanced distillation effect of seasonal sea-ice formation, which increases salinity through brine rejection during freezing near Antarctica, while decreasing salinity in the more northerly latitudes where the ice is blown by wind and subsequently melts [*Saenko and Weaver*, 2001]. Accelerated formation of SAMW-AAIW, consistent with heavy benthic foraminiferal $\delta^{13}C$ in intermediate depths [*Matsumoto et al.*,

2002; *McCorkle et al.*, 1998] would have enhanced the O_2 supply to the global thermocline by increasing flow rates.

[35] Although SAMW-AAIW is the single most important global source of O_2 to the thermocline [*Russell and Dickson*, 2003], the Northern Hemisphere middle- to high-latitude thermocline ventilation should also be enhanced under cold, windy conditions. However, it must also be recognized that the O_2 budgets of potential WCD zones in different locations will also depend on low-latitude O_2 sources, such as local intermediate water formation and diapycnal mixing of O_2-rich waters from above, as well as currently unresolvable possibilities of altered circulation pathways. These impacts would introduce additional spatiotemporal complexity, superimposed upon the long-term global trends. Furthermore, even if changes in O_2 supply were globally uniform, the response of geographically separated WCD zones to gradual changes in thermocline O_2 supply would be neither linear nor synchronous.

[36] This important corollary follows from the spatial complexity and temporal variability of marine export production (and hence OxD), which engenders a range of WCD thresholds as illustrated schematically in Figure 5. Some regions of the world ocean would be expected to experience consistently high OxD and be sites of significant WCD during all but the coldest and windiest periods (e.g., western Mexican margin, Figure 2 and schematically illustrated by line a in Figure 5), while others only experience enough OxD to instigate WCD during the warmest and calmest conditions (e.g. Peru, Figure 2, line b of Figure 5). It follows that contrasts in sensitivity to both O_2 supply and fluctuations in the local distributions of OxD should produce regional phase offsets in the onsets and cessations of denitrification among the different OMZs on millennial timescales. This critical feature of the proposed model is illustrated by the $\delta^{15}N$ curves sketched in the bottom panel of Figure 5. As a result, tuning of distant $\delta^{15}N$ records to each other on millennial timescales is unjustified, and time series analyses of multiple records must be interpreted cautiously.

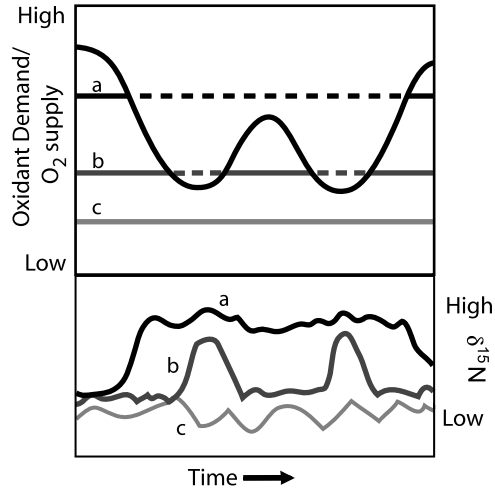

Figure 5. A schematic illustration showing expected temporal contrasts in the activity of WCD in three different water masses subjected to identical changes in (top) O_2 supply over time and (bottom) the local $\delta^{15}N$ records that would result. Each horizontal line in the top panel represents a hypothetical water mass that is subject to a constant oxidant demand (OxD) over time. Water mass "a" receives the greatest oxidant demand, while water mass "c" receives the least. The curved line represents the changing O_2 supply over time, driven by physical processes. The solid horizontal segments indicate time periods when oxygenation is sufficient to inhibit denitrification, while dashed horizontal segments indicate periods when oxygen is insufficient and denitrification is active. As shown, the onsets and cessations of denitrification are not exactly synchronous among the water masses, even in this highly idealized case in which local temporal variation of OxD is ignored, simply due to different threshold sensitivities to O_2 supply. Nonetheless, the $\delta^{15}N$ records follow the same general trends over long timescales.

3.8. Early Holocene $\delta^{15}N$ Maxima

[37] As mentioned earlier, all $\delta^{15}N$ records from within or near potential WCD zones show maxima during the early Holocene (Figure 2). We suggest two complementary mechanisms to explain a maximum in WCD after the LGM, followed by a decline to modern values.

[38] First, circum-Antarctic atmospheric and sea surface temperatures peaked [*Ikehara et al.*, 1997; *Mashiotta et al.*, 1999; *Masson et al.*, 2000] while sea ice extent reached a minimum near 11 to 10 kyr ago [*Hodell et al.*, 2001]. Thus O_2 supply to intermediate waters would have reached a minimum at this time. This minimum remained roughly unchanged until 5–6 kyr ago, when Southern Ocean temperatures began to decrease and sea ice extent expanded, thus increasing the O_2 supply and reducing the oxygen deficiency in distant denitrification zones. However, the Holocene climatic deterioration was relatively minor and it seems unlikely that a linear dependence on O_2 supply can be the sole explanation for the $\delta^{15}N$ decline.

[39] More importantly, it is likely that the deglacial increase in denitrification would have reduced global N:P because of the imperfect coupling of denitrification and fixation, as discussed above. The expansion of oceanic regimes limited by NO_3^- (i.e., those in which fixation is incapable of compensating N loss due to micronutrient limitation or inappropriate physical conditions) is likely to have reduced export productivity over the deglaciation, decreasing the OxD (the "slow" feedback of *Codispoti* [1989]). Because WCD zones occur near large upwelling-driven ecosystems that are prone to nitrate limitation, this feedback would be effective in reducing OxD in the most sensitive regions.

[40] As an example, consider the ETNP. Today, in the heart of the denitrification zone, nitrate concentrations average roughly 30 μmol/kg, while phosphate concentrations are ~2.5 μmol/kg (a nitrate deficit of 10 μmol/kg). If oxygen supply were sufficient during the LGM to completely inhibit water column denitrification, immediately upwelled water might be expected to have an N/P near 16; thus, we would have concentrations of 40 μmol/kg NO_3^- and 2.5 μmol/kg PO_4^{3-}. If the oxygen minimum were then to become suboxic early in the deglaciation, and the denitri-

fication zone were to intensify to roughly double that of today, denitrified waters would contain only 20 μmol/kg NO_3^-. When welled up, these waters would only be able to support half the export production of their glacial equivalents in the absence of immediate N-fixation.

[41] Such a negative feedback between denitrification and OxD would serve to stabilize the system once the O_2 supply had ceased its downward trend. In effect, global OxD would readjust to changes in O_2 supply over 10^2–10^3 years in order to bring the N system into balance. We speculate that this homeostatic mechanism may be responsible for maintaining the global OxD in near-balance with O_2 supply over long timescales, preventing widespread water column anoxia despite variable environmental conditions.

[42] Denitrification in bottom sediments could also have a complicated effect on the N balance of the ocean via the change in the locus of organic matter oxidation due to sea level fluctuations. As discussed by *Christensen et al.* [1987], the exposure of ~75% of the world's continental shelves during glacial lowstand would have reduced the amount of remineralization in shelf sediments, and shifted more of the remineralization burden (hence OxD) to the water column. As long as O_2 supply to the thermocline remained vigorous, this OxD would have been largely satisfied by dissolved O_2. However, during the deglaciation, the decrease in O_2 supply would have preceded the resumption of sediment denitrification, as shelves were not yet flooded, causing an intervening period of high water column OxD and declining O_2. The subsequent decline in Holocene $\delta^{15}N$ could then reflect the short-circuiting of water column remineralization by the "trap" of submerged continental shelves.

[43] The early Holocene $\delta^{15}N$ maximum highlights an important feature of the marine nitrogen system: productivity feedbacks on WCD are likely to complicate the temporal-spatial pattern, such that the global aggregate rates of WCD are not strictly correlated with temperature and winds. The accumulated evidence shows that, instead, WCD is maximal during the transitions from warm to cold periods as the marine nitrogen cycle adjusts to the diminishing oxygen supply.

4. Summary and Conclusions

[44] This paper has presented a parsimonious reconciliation of diverse nitrogen isotope records on long timescales (>10 kyr), which calls on a strong temporal coupling of denitrification to N fixation as has been suggested previously [*Ganeshram et al.*, 2002]. As the fundamental driver, a direct link is proposed between oceanic surface conditions and the oxygenation of the global permanent thermocline, which modulates the nutrient dynamics of the marine biosphere. This relatively simple, physical mechanism has the potential to explain much of the variability in sedimentary $\delta^{15}N$ records as well as some contribution to the known atmospheric pCO_2 and pN_2O fluctuations [*Flückiger et al.*, 2004] over the past 200 kyr. Furthermore, it can be investigated through modeling studies, and readily tested by developing records of thermocline water temperature and ventilation-related parameters in the 200–1000 m depth range.

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